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INFLUENCE OF SILICON DIOXIDE ON THE EQUILIBRIUM OF
LIQUID IRON WITH SIMPLEST BASIC SLAGS

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It was established by several investigators that expressions:

$$\frac{(MeO)(Fe)}{(FeO)(Me)} = K' \quad (1)$$

in which (MeO) and (FeO) are molar fractions of oxides in slag and \bar{Me} and \bar{Fe} -- atomic fractions in the metal phase, remain more or less constant for a given temperature under conditions of equilibrium in systems Fe, Me, O/FeO, MeO when Me is represented by Mn [1], Ni [2] and Co [3]. Analogous results were obtained also for the system Ni, Co, O/NiO, CoO. According to Gerasimov [4], it follows from experiments by Fotters and Chipman [5] that for Me = Ca the ratio

$$\frac{[\%O]}{(FeO)} = L' \quad (2)$$

also varies very little with changing slag composition.

On the other hand, introduction of SiO₂ has a great effect on K' and L' for the same Me's. It is easily noticeable that the magnitude and direction of variations of K' with the same admixture of SiO₂ depend on the size of the cation Me²⁺. For $r_{Me^{2+}} > r_{Fe^{2+}}$ the value of K' grows with an increase of the SiO₂ content; inversely, for $r_{Me^{2+}} < r_{Fe^{2+}}$ it falls down, and the less this diminution, the nearer to $r_{Fe^{2+}}$ is the cation. For example, for the pair Mn, Fe ($r_{Mn^{2+}} = 0.92$ A.U., $r_{Fe^{2+}} = 0.83$ A.U.) the value of K' greatly increases [1] with introduction of SiO₂. However, for Ni, Fe ($r_{Ni^{2+}} = 0.78$ A. U.) it goes down [2, 6], this decrease being slower than

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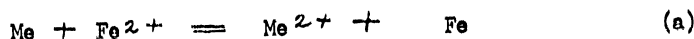
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the increase in the case of Mn, Fe. For Co, Fe ($r_{Co^{2+}} = 0.92 \text{ A.U.}$) the decrease of K' is of the least magnitude [3]. The system Ni, Co behaves the same way. The value of K' in this system goes down somewhat slower than in the case of Ni, Fe. Finally, the data of Chipman and his coworkers [5, 7], analyzed by A. Samarin, L. Shvartsman and M. Temkin [8], V. Kozheurov (unpublished work) and A. Keinman [9], showed that the value of:

$$\frac{[\%O]}{N_{Fe^{2+}} \cdot N_{O^{2-}}} = L' \quad (3)$$

(where N 's are ionic fractions of iron and oxygen in the slag of the system in which $Me = Ca$) sharply increases with the increase of the SiO_2 content. Probably, this also is connected with the great difference in radii of cations ($r_{Ca^{2+}} = 1.06 \text{ A.U.}$).

These regularities may be explained by referring to the electrolytical theory. Molten slags represent strong electrolytes [10, 11]. Therefore the equilibriums under consideration may be expressed by the following equations:



Expressions for equilibrium constants may be simplified because the metal phase is close to the ideal solution. Such a possibility is substantiated by the absence of stable liquid intermetallic compounds of iron with Mn, Co and Ni, the narrow lens between their lines of liquidus and solidus [12], the comparatively low solubility of oxygen in iron and negligible solubility of calcium. On account of all these factors the activities of Fe, Mn, Co and Ni may be replaced by atomic fractions and the activity of oxygen by its percentage.

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The most convenient method for expressing ion activities in slag is a model suggested by M. Temkin [13]. This model depicts the basic moment characterizing the arrangement in molten electrolytes, namely the closest adjacency of ions with opposite signs; in other relations all like ions in it are completely levelled. In such a perfect ion solution the activity of an ion is equal to its ion fraction, i.e., to the ratio between the number of ions of a given kind and the total number of ions with the same sign. Let us introduce coefficients of ion activity for evaluating the deviation of slag from the perfect ion solution. These coefficients characterize nonequivalence of similarly charged particles and their specificity.

Hence, the following expressions deduced from equilibrium constants of processes (a) and (b) may be written:

$$\frac{N_{Me^{2+}} \cdot f_{Me^{2+}} \cdot [Fe]}{N_{Fe^{2+}} \cdot f_{Fe^{2+}} \cdot [Me]} = K = \text{const}, \quad (4)$$

$$\frac{[\% O] [Fe]}{N_{Fe^{2+}} \cdot f_{Fe^{2+}} \cdot N_{O^{2-}} \cdot f_{O^{2-}}} = L = \text{const} \quad (5)$$

It is easy to notice that, in the presence of MeO and absence of SiO_2 in slag, $N_{Fe^{2+}} = (FeO)$ and $N_{Me^{2+}} = (MeO)$. Therefore, comparison of equations (1) and (4) leads to the conclusion that strict constancy of K' is possible only when the ratio of activity coefficients of Fe^{2+} and Me^{2+} does not depend on composition, as for example, if MeO and FeO form the ideal ion solution in which the interaction energies of both cations with O^{2-} are similar. Equal charges and nearness of sizes of the cations Fe^{2+} , Mn^{2+} , Co^{2+} and Ni^{2+} permit to assume that this condition will be approximately observed, especially for the pair Fe, Co. However some differences in radii and polarities of other cation pairs may result in a certain inconstancy of K' .

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In particular, this inconstancy may be expected in the Fe, Mn pair, Fe, Ni and Co, Ni. It is easy to show that, at similar coordination numbers, dependence of K' on composition will be here determined by the extent of difference between the cation energy of interaction with O^{2-} in the unsymmetrical situation $Me_1^{2+} - O^{2-} - Me_2^{2+}$ and that energy for the symmetrical situation $Me_1^{2+} - O^{2-} - Me_1^{2+}$. Insufficient accuracy of experiments prevented further clarification of this dependence.

For slag, composed of CaO, FeO, the atomic fraction of iron in metal and the ionic fraction of oxygen in slag are equal to one. Comparison of equations (2) and (5) shows that L' will be strictly constant if the product $f_{Fe^{2+}} f_{O^{2-}}$ does not vary with slag composition. This could happen if actions of Ca^{2+} and Fe^{2+} with O^{2-} were similar. But the difference in sizes and polarizabilities of Ca^{2+} and Fe^{2+} is the greatest in comparison to other pairs. Therefore, the clearest dependence of L' on slag composition could be expected here. However, in the experimentally investigated region ($N_{Fe^{2+}} \gg N_{Ca^{2+}}$) the activity coefficients $f_{Fe^{2+}}$ and $f_{O^{2-}}$ vary in opposite directions. Actually, here the part of iron ions is in positions $Fe^{2+} - O^{2-} - Ca^{2+}$. Since interaction of O^{2-} with Fe^{2+} is greater than that of O^{2-} with Ca^{2+} , the negative charge O^{2-} will approach the positive charge Fe^{2+} . The energy of interaction of Fe^{2+} with O^{2-} will be greater here than in situations $Fe^{2+} - O^{2-} - Fe^{2+}$. As the number of the latter grows with $N_{Fe^{2+}}$, $f_{Fe^{2+}}$ must grow also. On the other hand, the energy of interaction of O^{2-} with cations is greater in the states $Fe^{2+} - O^{2-} - Fe^{2+}$ than in the situations $Fe^{2+} - O^{2-} - Ca^{2+}$. For this reason, with increasing $N_{Fe^{2+}}$ the coefficient $f_{O^{2-}}$ will go down but more slowly than $f_{Fe^{2+}}$ will grow. Thus, the increase of L' with $N_{Fe^{2+}}$ is weakened; L' may vary non-monotonically with $N_{Fe^{2+}}$ and may have an extreme in the region experimentally accessible.

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Data obtained by Chipman and his collaborators [5, 7] may confirm to a certain extent all regularities discussed in this article.

The influence of SiO_2 on K' and L' may be qualitatively explained in the following way. For a given ratio of MeO and FeO , introduction of SiO_2 into a melt leads to the appearance of SiO_4^{4-} and disappearance of a double number of ions O^{2-} . Since the radius of SiO_4^{4-} is approximately equal to $2r_{\text{O}^{2-}}$, the energy of its interaction with cations will be less than twice the energy of interaction of cations with O^{2-} . Therefore the introduction of SiO_2 decreases the linkage of cations with the melt and raises their activity coefficients, and this increase will be greater for cations with smaller radii. Thus, in agreement with the experiment, the ratio $f_{\text{Fe}^{2+}}/f_{\text{Me}^{2+}}$ and K' must grow with the concentration increase of SiO_2 for $r_{\text{Me}^{2+}} > r_{\text{Fe}^{2+}}$ and they must decrease for $r_{\text{Me}^{2+}} < r_{\text{Fe}^{2+}}$. Further, since in the first approximation the number of cations for every O^{2-} may be assumed the same as in the absence of SiO_2 , then the $f_{\text{O}^{2-}}$ remains almost the same as in the melt MeO , FeO . Therefore, the change of L' upon the addition of SiO_2 is determined mainly by $f_{\text{Me}^{2+}}$. As the latter increases with the increase of the SiO_2 content, L' ~~is~~ also increases.

However, it is still not clear why the effect of changes in composition of the melt MeO , FeO is weak and revealed only for cations with sharply differing sizes and polarizabilities (Fe^{2+} and Ca^{2+}), while the addition of SiO_2 has a very sharp effect on the very same cation pairs. Evidently, in addition to the above mentioned causes which may be conditionally considered as entirely electrostatic ones, an essential role is played by the different stability of SiO_4^{4-} in the presence of Me^{2+} and Fe^{2+} . Each cation deforms to a certain extent adjacent SiO_4^{4-} up to the separation of O^{2-} from some of them. The cation with the greater energy of interaction with O^{2-} (Fe^{2+} , for example) destroys SiO_4^{4-} more intensively and surrounds itself with

CONFIDENTIAL

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anions O^{2-} . On account of this, SiO_4^{4-} is driven to the weak cation (Ca^{2+} , for example). Solely static distribution of anions SiO_4^{4-} and O^{2-} around Me^{2+} and Fe^{2+} is disrupted and greater regulation in the distribution of particles arises in the melt than is foreseen by the theory of perfect ionic solutions [14].

The "strong" cation (Me_{II}^{2+}) causes less numerous rearrangements of anions and the increase in number of rearrangements with the increase of SiO_2 content is smaller as compared to the "weak" cation (Me_I^{2+}). Therefore the activity of Me_{II}^{2+} is reduced more slowly than the product of ion fractions ($N_{Me}^{2-} \cdot N_{O^{2-}}$). As a result, additional "rearrangement" coefficients of activity appear, growing with the increase of the SiO_2 content and causing an increase of L' . On the other hand, since by the same token a $Me_{II}O$ is reduced more slowly than a $Me_I O$, the ratio of rearrangement activity coefficients $f_{Me_{II}^{2+}}/f_{Me_I^{2+}}$ and K' also increase with the increase of SiO_2 .

Thus, additional regulation of ions in the melt, conditioned by the difference in energies of interaction of cations with O^{2-} , has an effect on the values of K' and L' in the same direction as the effect of the entirely electrostatic factors. Being superimposed on each other, both these factors lead to the greater effect which is observed experimentally.

The concepts developed here for silicates may be applied also to systems containing other complex anions, as for example aluminates, phosphates and ferrites.

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- 7 -

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